DEVELOPMENT ON PRE-HEATING SYSTEM FOR AUTOTHERMAL REFORMER FOR FUEL CELL APPLICATION

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I declared that this thesis entitled ‘Development of Preheating System for Autothermal Reformer for Fuel Cell Application’ is the result of my own research except as cited in the references. The thesis has not been accepted for any degree is not concurrently submitted candidature of any degree.

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Special dedicated to my beloved mother and father

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ABSTRACT

The objective of this research is to investigate the performance of catalytic combustion of hydrogen by using Pt/Al_2O_3 in different weight loading catalyst ranged from 0.06 to 0.2 gram in assisting the catalytic combustion of methane experimentally. 1 wt% and 3 wt% platinum catalyst used to determine the performance of catalytic combustion of hydrogen. The platinum supported with alumina to increase the area of platinum to faster the reaction and to reduce cost. The behavior of hydrogen has been studied accordingly based on their auto ignition in room temperature and atmospheric pressure when contact with platinum with air in the range of lower and upper flammability limits. Sets of range from 72% to 97% fuel to air ratio were used for the experiment. Different weight loading of catalyst and catalyst weight percent of Pt in alumina gave various performances and the effect of air/fuel ratio was observed as well to get the best result. The catalytic combustion of hydrogen was a complete combustion and could reach up to 450°C. The experiment held in vertical single bed reactor whereby the exit temperature of catalytic combustion of hydrogen was recorded for performance comparison. The best performance was hydrogen flow rate set to 772.8 ccm and air set to 272.16 ccm with 1wt% Pt and weight loading 0.1gram which gave temperature of 459°C because the effect of larger surface reaction.

ABSTRAK

Objektif kepada penyelidikan ini adalah untuk menyiasat perlaksanaan pembakaran bermangkin hidrogen dengan menggunakan Pt/Al_2O_3 dalam kandungan pemangkin yang berbeza 0.06 gram sehingga 0.2 gram dalam membantu pembakaran bermangkin metana secara eksperimen. 1 wt% and 3 wt% katalis platinum digunakan untuk dalam pembakaran bermangkin hidrogen. Platinum disokong oleh alumina untuk meningkatkan luas permukaan platinum bagi mempercepatkan tindak balas dan mengurangkan kos. Tindakbalas hidrogen telah diselidik secara meluas bahawa terbakar secara automatik pada suhu bilik dan tekanan atmosfera apabila bersentuh dengan platinum dengan kehadiran udara pada had atas dan bawah keterbakaran. Pada had 72% sehingga 97% nisbah bahan bakar kepada udara digunakan dalam eksperimen ini. Berbeza kandungan berat katalis dan berbeza peratus katalis platinum akan memberikan keputusan yang berbeza dan kesan perubahan nisbah bahan bakar kepada udara juga di perhatikan untuk keputusan yang terbaik. Pembakaran bermangkin hidrogen adalah lengkap dan boleh mencecah kepada suhu 450°C. Eksperimen dijalankan didalam reactor kaca secara menegak dimana suhu yang terhasil direkodkan sebagai perbandingan keputusan. Prestasi terbaik adalah pada kadar aliran hydrogen 772.8 ccm dan udara 272.16 ccm dengan 1wt% Pt dan berat 0.1gram mencatatkan suhu 450°C disebabkan kesan luas permukaan tindak balas yang lebih besar.

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LIST OF ABBREVIATIONS

AFC	-	Alkaline fuel cell
Al_2O_3	-	Alumina
ATR	-	Autothermal reformer
CCM	-	Centimeter cubit minute
CST	-	Catalytically stabilized combustion
CHP	-	Combined heat power
CH_4	-	Methane
C_2H_6	-	Ethane
C_3H_8	-	Propane
C_4H_{10}	-	Butane
CO	-	Carbon monoxide
CO_2	-	Carbon dioxide
CPO	-	Catalytic partial oxidation
H_2	-	Hydrogen
H_2O	-	Water
MCFC	-	Molten carbonate fuel cell
PAFC	-	Phosphoric acid fuel cell
Pd	-	Palladium
PEMFC	-	Proton exchange membrane fuel cell
POX	-	Partial oxidation
LPG	-	Liquefied petroleum gas
Pt	-	Platinum
Pt/Al2O3	-	Platinum alumina
SPFC	-	Solid polymer fuel cell
SOFC	-	Solid oxide fuel cell

UPS	-	Uninterrupted power supply
WGS	-	water gas shift

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CHAPTER 1

INTRODUCTION

1.1 Background of study

A fuel cell by definition is an electrical cell, which unlike storage cells can be continuously fed with a fuel so that the electrical power output is sustained indefinitely (Reed, 1995).

A fuel cell consists of two electrodes sandwiched around an electrolyte. Oxygen passes over one electrode and hydrogen over the other, generating electricity, water and heat. Hydrogen fuel is fed into the anode of the fuel cell. Oxygen enters the fuel cell through the cathode. Encouraged by catalyst, the hydrogen atom splits into a proton and an electron, which take different paths to the cathode. The proton passes through the electrolyte. The electrons create a separate current that can be utilized before they return to the cathode, to be reunited with the hydrogen and oxygen in a molecule of water.

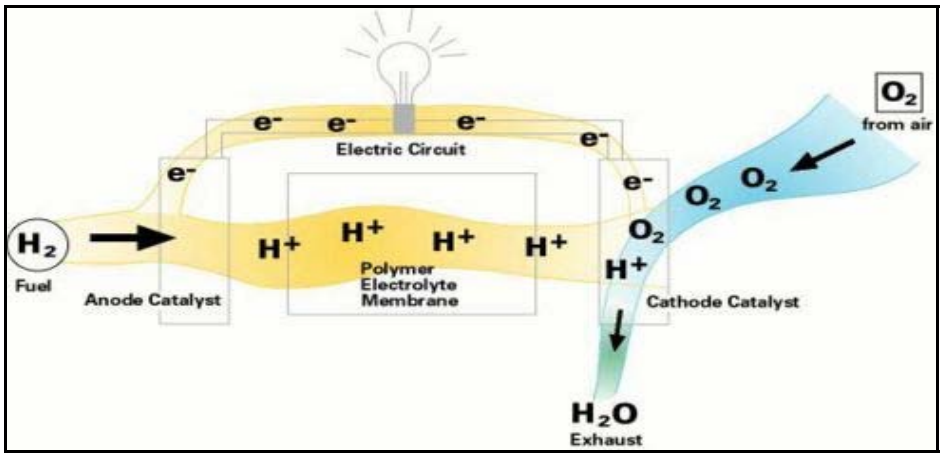

Figure 1.1: Working principle of fuel cell

In general, fuel cells are classified according to the electrolyte use. There are the alkaline fuel cell used in space vehicle power system, the phosphoric acid fuel cell (PAFC) used in both road transportation and stationary engines, the solid polymer fuel cell (SPFC) also used in both road transportations and stationary engines, the molten carbonate fuel cell (MCFC) used in stationary engines and the solid oxide fuel cell (SOFC) used only in stationary engines (Chen and Elnashaie, 2004).

A fuel cell system which includes a fuel reformer can utilize the hydrogen from any hydrogen fuel – from natural gas to methanol, and even gasoline.

The three major approaches for the conversion of hydrocarbon fuels to hydrogen are steam reforming, partial oxidation and auto thermal reforming. The last mention is a chemical combination of steam reforming and partial oxidation. Argonne National Laboratory has articulated the advantages of the auto thermal reforming (ATR) process for many applications that face constraint on size, duty cycle such as in automotive power plant. In the ATR process, fuel is co-fed with steam and air, and the feed composition is adjusted to maintain a slightly exothermic reaction.

In general, fuel cell can be used for a wide variety of applications, the most important of which are as power source for vehicle, as a stationary power source and as power sources for portable devices. Natural gas and propane are attractive for stationary

applications since they are low-cost fuels and the infrastructure for their transportation already exists (Wang et al., 2005).

1.2 Problem statement

Conventional autothermal reformer have disadvantage, particularly with respect to fuel cell-related applications. Conventional autothermal reformer and associated heat recovery equipment tend to be quite large, which impacts material cost and overall manufactured cost. This is especially disadvantageous in vehicular application, where space is also at a premium.(Faye *et.al*,2004).

1.3 Objective of the project

a) Assemble and fabricate test rig on preheating system using catalytic combustion for ATR.

b) Study on performance testing by using platinum alumina (Pt/Al_2O_3) as catalyst and hydrogen as fuel in preheating process.

1.4 Scope of research

Scope of this research is to fabricate the rig for pre-heating system at Autothermal reformer and make performance test by different weight loading catalyst of 1% and 3% Pt in alumina and different fuel to air ratio range 15% to 75% to achieve minimum temperature of catalytic combustion of hydrogen above 368°C

CHAPTER 2

LITERATURE REVIEW

2.1 History of fuel cell

The history of fuel was discovered by William Grove in early 1839 by reversing water electrolysis to generate electricity from hydrogen and oxygen. A fuel cell does not need recharging, it operates quietly and efficiently, and when hydrogen is used as fuel, it generates only power and drinking water. Thus it is a called zero emission engine. Grove's fuel cell was a fragile apparatus filled with dilute sulfuric acid into which platinum electrodes were dipped.

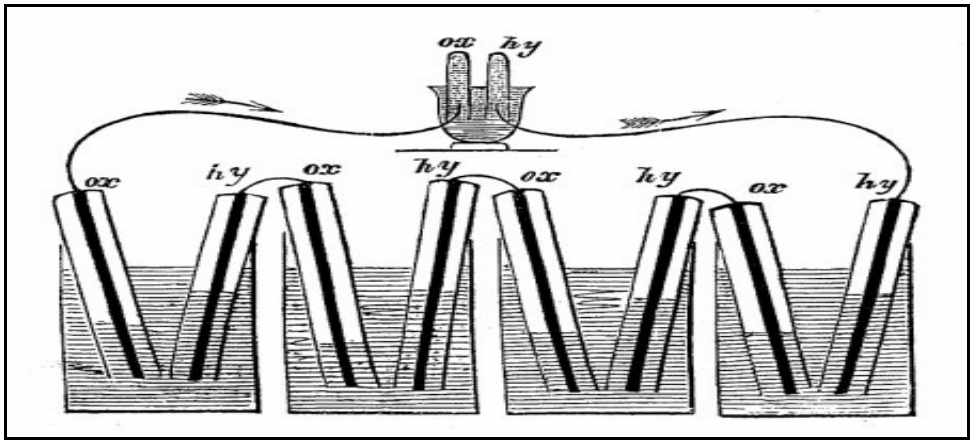

Figure 2.1: William Grove's 'gas battery', the first fuel cell.

2.2 Type of fuel cell

Fuel cells are a family of technologies. Fuel cell types are characterized by their electrolytes and temperature of operation. (Gregor, 2003).

2.2.1 Proton exchange membrane

Proton exchange membrane (PEM) fuel cells have a solid polymer membrane as an electrolyte. Due to membrane limitations, PEMs usually operate at low temperatures (60-100°C/140-212°F), but new developments have produced higher temperature PEMs (up to 200°C/392°F). Since platinum is the most chemically active substance for low temperature hydrogen separation, it is used as the catalyst. Hydrogen fuel is supplied as hydrogen gas or is reformed from methanol, ethanol, natural gas or liquefied petroleum gas and then fed into the fuel cell. The power range of existing PEMs is about 50W to 150kW. The advantages of using PEM fuel cells include:

a) Low weight and volume with good power-to-weight ratio,
b) Low temperature operation, so less thermal wear to components, and
c) Quick starts, with full power available in minutes or less.

These advantages make PEMs well-suited to automotive and specialty vehicle applications such as scooters and forklifts. Many on-road trials are providing information to make PEMs competitive with internal combustion engines. Quick-starting PEMs can also provide back-up power to telecommunications and other sites requiring uninterrupted power supplies (UPS). PEMs additionally offer efficient operation – up to 50% electrical efficiency for the fuel cell itself and over 85% total efficiency when waste heat is captured for small-scale space and water heating (combined heat and power, or CHP). Hundreds of CHP and UPS PEM units have been deployed in demonstrations, and a number of units are now available for sale.

Several challenges face PEMs. Platinum catalysts are expensive and also subject to CO poisoning from hydrocarbon fuels, so catalyst improvements, non-precious metal catalysts and other alternatives are under investigation. Membranes more resistant to chemical impurities are also being developed. Alternate storage methods, such as metal hydrides and carbon nanostructures, may address hydrogen storage limitations preventing fuel cell cars from achieving typical driving range (300-400 miles/tank). Cold starts from frozen internal water are improving – a US Department of Energy goal is to achieve cold starts from -20°C (-4°F) in 30 seconds or less.

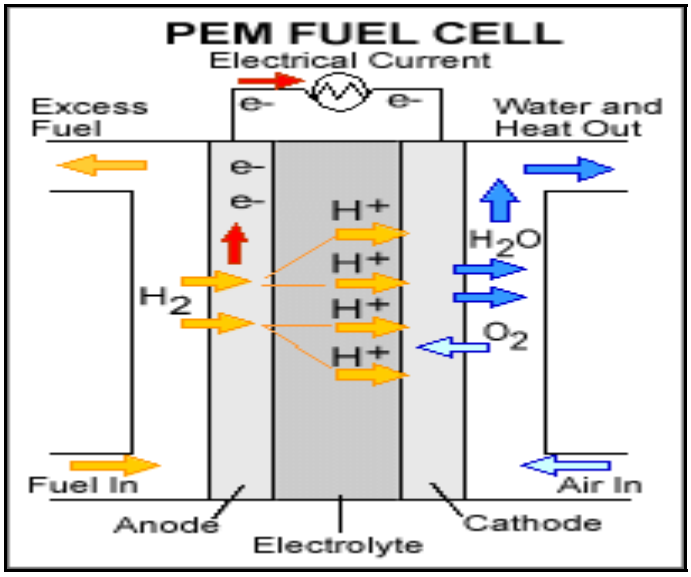

Figure 2.2: Schematic view of PEM fuel cell.

2.2.2 Direct methanol fuel cells

Direct methanol fuel cells (DMFCs) differ from PEMs because they use unreformed liquid methanol fuel rather than hydrogen. DMFCs operate at slightly higher temperatures than PEMs (50-120°C/120-248°F) and achieve around 40% efficiency. Since they are refuelable and do not run down, DMFCs are directed toward

small mobile power applications such as laptops and cell phones, using replaceable methanol cartridges at power ranges of 1-50 W. Many of the major electronics companies are demonstrating miniature DMFCs powering their equipment and smaller fuel cell companies are partnering with military and communications contractors. The United Nations recently declared that methanol cartridges were safe for shipment in airplane cargo holds. Developers are currently addressing membrane corrosion, fuel crossover and miniaturization challenges. DMFCs are poised for widespread commercial availability in 2006, and some companies, such as SFC Smart Fuel Cell AG, are selling products now.

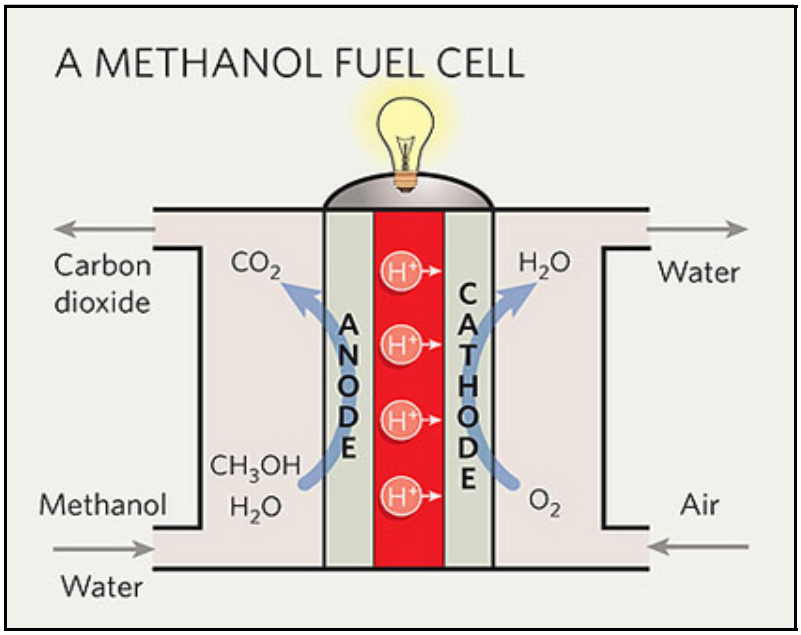

Figure 2.3: Schematic view of methanol fuel cell.

2.2.3 Phosphoric acid fuel cell

The phosphoric acid fuel cell (PAFC) is the fuel cell technology, with the greatest experience in consumer applications. UTC Fuel Cells (formerly ONSI and International Fuel Cells) paved the way for the technology, selling systems since the early 1990's and recently reaching the milestone of more than one billion kilowatt-hours of energy with its PureCell™ 200 power plant solution. PAFCs use liquid phosphoric acid as an electrolyte with a platinum catalyst. Anode and cathode reactions are similar to PEMs, but operating temperatures are slightly higher (150-200°C/302-392°F) making them more tolerant to reforming impurities. PAFCs use hydrocarbon sources such as natural gas, propane or waste methane. PAFCs are typically used for medium to large-scale stationary power generation, attaining a 36-42% electrical efficiency and an overall 85% total efficiency with co-generation of electricity and heat. The power range of existing PAFCs is 25-250 kW. However, if several units are linked, PAFCs can achieve a combined power output greater than 1 MW (an 11 MW PAFC power plant is operating in Japan).

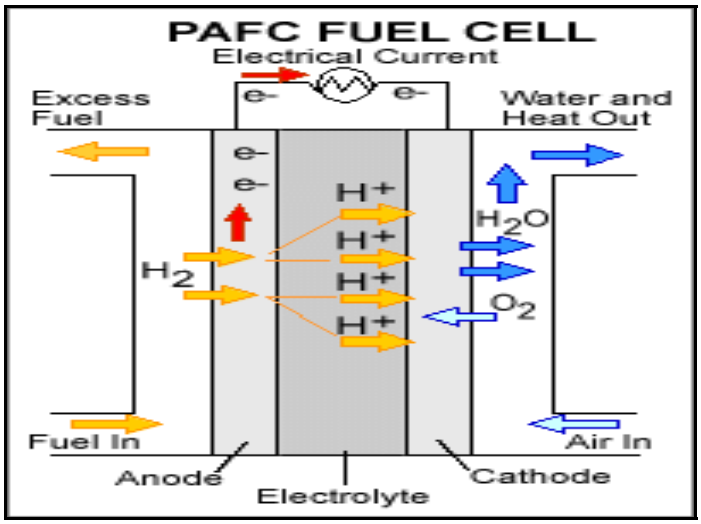

Figure 2.4: Schematic view of PAFC fuel cell.

2.2.4 Alkaline fuel cells

Fast-starting alkaline fuel cells (AFCs) have been used by NASA to produce power and drinking water for astronauts since the 1960s Gemini missions. AFCs operate in an electrolyte solution of potassium hydroxide and can use a variety of non-precious metal catalysts at operating temperatures of 23-250°C (74-482°F). Fuelled by hydrogen gas, AFCs have a high chemical reaction rate and offer an electrical efficiency of 60-70%. However, AFCs are poisoned easily by small quantities of carbon dioxide, so they are mostly used in controlled aerospace and underwater applications. AFCs in Space Shuttle applications produce 12 kW of power.

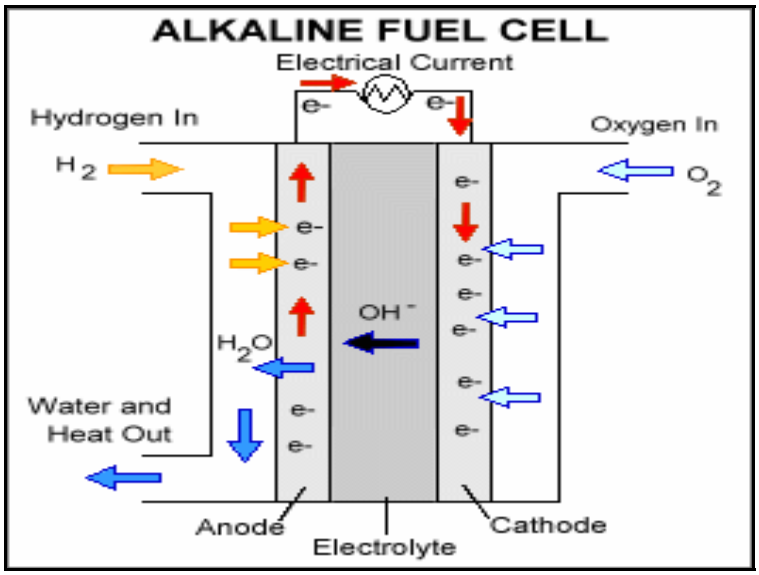

Figure 2.5: Schematic view of alkaline fuel cell.

2.2.5 Solid oxide fuel cells

Solid oxide fuel cells (SOFCs) are one of the high temperature fuel cells, operating at 800-1000 °C (1472-1832°F) High temperature operation eliminates the need for precious metal catalysts and can reduce cost by recycling the waste heat from internal steam reformation of hydrocarbon fuels. SOFCs are tolerant to CO poisoning, allowing CO derived from coal gas to also be employed as source of fuel. These fuel cells use a solid ceramic electrolyte and produce a power output of 2-100 kW and can attain 220 kW-300 kW when used in a SOFC/gas turbine hybrid system. Demonstrated electrical efficiencies are 45-55%, with total efficiencies of 80-85% with cogeneration of waste heat. SOFCs are well-suited for medium-to-large scale, on-site power generation or CHP (hospitals, hotels, universities), and are also being marketed for telecommunications back up and as auxiliary power units (APUs) for military vehicle on-board equipment.

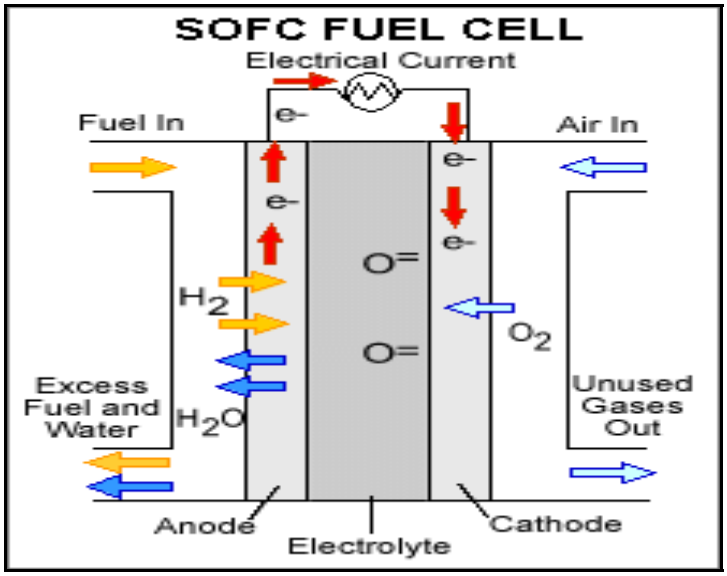

Figure 2.6: Schematic view of SOFC fuel cell.

2.2.6 Molten carbonate fuel cells

Molten carbonate fuel cells (MCFCs) operate at 600-750°C (1112-1382°F) and use a molten alkali carbonate mixture for an electrolyte. MCFCs typically range between 75-250 kW, but when using combined units, have produced up to 5 MW of power. Electrical efficiencies are 50-60%, with total efficiencies of 80-85% with cogeneration of waste heat. To date, MCFCs have operated on hydrogen, carbon monoxide, natural gas, propane, landfill gas, marine diesel, and simulated coal gasification products.

The challenges to both SOFC and MCFC development include slow start up, strong thermal shielding requirements, and difficulty in developing durable materials for the high temperature operating environment. Developers and the US government (Solid State Energy Conversion Alliance) are also working on lower cost, greater durability, low-temperature SOFCs (about 800°C), as well as more powerful SOFC/gas turbine hybrids (1 MW or greater). Current MCFC research focuses on reduction of size and cost, as well as possible integration with gas turbines to increase performance.

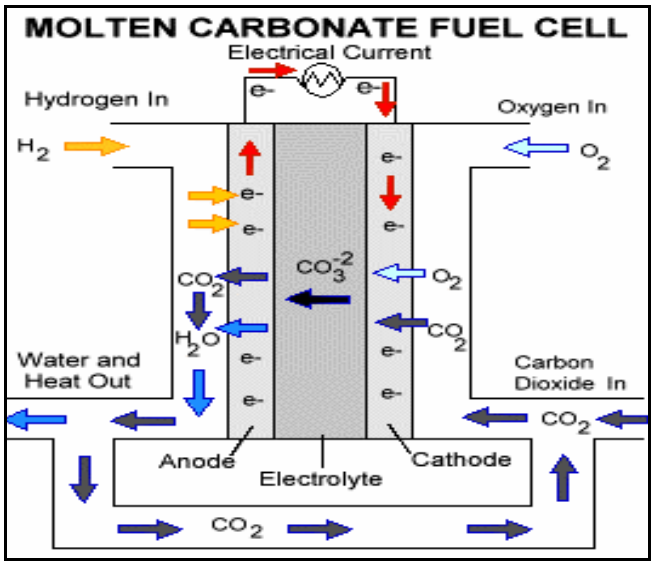

Figure 2.7: Schematic view of molten carbonate fuel cell.

Table 2.1: Summary for different type of fuel cell (Appleby and Foulkes, 2004).

	PEFC	AFC	PAFC	MCFC	SOFC
Electrolyte	Hydrated Polymeric Ion Exchange Membrane	Mobilized or Immobilized Potassium Hydroxide in asbestos matrix	Immobilized Liquid Phosphoric Acid in SiC	Immobilized Liquid Molten Carbonate in $LiALO_2$	Perovskites(ceramics)
Electrodes	Carbon	Transition metal	Carbon	Nickel and Nickel Oxide	Perovskite and Metal Cement
Catalyst	Platinum	Platinum	Platinum	Electrode material	Electrode material
Interconnect	Carbon or metal	Metal	Graphite	Stainless steel or Nickel	Nickel, ceramic or steel
Operating Temperature (°C)	40-80	65-220	205	650	600-1000
External Reformer For Hydrocarbon Fuels	Yes	Yes	Yes	No, for some fuels	No, for some fuels and cell design
External Reformer for Hydrocarbon Fuels	Yes, plus purification to remove trace CO	Yes, plus purification to remove CO and CO_2	Yes	No	No
Prime Cell Components	Carbon-based	Carbon-based	Graphite-based	Stainless-based	Ceramic
Product Heat Management	Process Gas + Liquid Cooling Medium	Process Gas + Electrolyte Circulation	Process Gas +Liquid Cooling medium or steam	Internal Reforming + Process Gas	Internal Reforming + Process gas

2.3 Production of hydrogen

Fuel cells generally run on hydrogen, but any hydrogen-rich material can serve as a possible fuel source. This includes fossil fuels – methanol, ethanol, natural gas, petroleum distillates, liquid propane and gasified coal. The hydrogen is produced from these materials by a process known as reforming. This is extremely useful where stored hydrogen is not available but must be used for power, for example, on a fuel cell powered vehicle.

There are three basic reformer designs are being evaluated for fuel cells for use in vehicles: steam reforming, partial oxidation and auto-thermal reforming. Steam reformers combine fuel with steam and heat to produce hydrogen.

The heat required to operate the system is obtained by burning fuel or excess hydrogen from the outlet of the fuel cell stack. Partial oxidation reformers combine fuel with oxygen to produce hydrogen and carbon monoxide. The carbon monoxide then reacts with steam to produce more hydrogen. Partial oxidation releases heat, which is captured and used elsewhere in the system. Auto-thermal reformers combine the fuel with both steam and oxygen so that the reaction is in heat balance.

2.3.1 Steam reforming

Steam reforming of methane from natural gas is the standard way of producing hydrogen on an industrial scale. It is therefore of general importance to a hydrogen economy. In addition, smaller scale methane steam reformer have been developed to provide hydrogen for stationary power systems based on low-temperature fuel cell, Proton Exchange Membrane Fuel Cell (PEMFC) and Phosphoric Acid Fuel Cell (PAFC).

The methane steam reforming is described by:

$CH_4 + H_2O \rightarrow CO + 3H_2 \qquad \Delta H = 206 kjmol^{-1}$ [2.1]

Methane steam reforming is usually catalyzed by nickel (Ridler and Twigg, 1996) at temperature between 750-1000°C, with excess steam to prevent carbon deposition on the nickel catalyst (Trimm and Onsan, 2001).

2.3.2 Partial oxidation

The second important reaction for generating hydrogen on an industrial scale is partial oxidation (POX). It is generally employed with heavier hydrocarbons (Dams, 1996) or when special preferences exist because certain reactants (for example, pure oxygen) are available within a plant. It can be seen as oxidation with less than the stoichiometric amount of oxygen for full oxidation to the stable end products, carbon dioxide and water.

For example, for methane:

$CH_4 + 1/2O_2 \rightarrow CO + 2H_2 \qquad \Delta H = -36\ kJmol^{-1}$ [2.2]

and/or

$CH_4 + O_2 \rightarrow CO_2 + 2H_2 \qquad \Delta H = -319\ kJmol^{-1}$ [2.3]

2.3.3 Auto thermal reforming

Autothermal reforming (ATR) is a process in which both steam and air are introduce to be the fuel. Compared to steam reforming, less water needed for Autothermal reforming. In addition, the heat of steam reforming is provided by the partial oxidation of fuel. Thus, no complex heat management needed, and system design became a little simple.

Steam and auto thermal reforming reaction of LPG (propane/butane) over highs surface area Ce_2O (Ce_2O_2 (HAS)) under solid oxide fuel (SOFC) operating condition was studied. The major consideration in the auto thermal reforming operation is the inlet O_2/LPG molar ratio, as the presence of too high an oxygen concentration could oxidize hydrogen and carbon monoxide, produced from the steam reforming, to steam and carbon dioxide. A suitable O/C molar ratio for auto thermal reforming on CeO_2 (HAS) been observed to be 0.6. (Laosiripojana et al. 2005).

2.4 Hydrogen from natural gas

Natural gas is a gaseous fossil fuel consisting primarily of methane but including significant quantities of ethane, butane, propane, carbon dioxide, nitrogen, helium and hydrogen sulphide. It is found in oil fields and natural gas fields and in coal beds (as coal bed methane). When methane-rich gases are produced by the anaerobic decay of non-fossil organic material, these are referred to as biogas. Sources of biogas include swamps, marshes, and landfills (see landfill gas), as well as sewage sludge and manure by way of anaerobic digesters, in addition to enteric fermentation particularly in cattle. Natural gas is often informally referred to as simply gas, especially when compared to other energy sources such as electricity. Before natural gas can be used as a fuel, it must undergo extensive processing to remove almost all materials other than methane. The by-products of that processing include ethane, propane, butanes, pentanes and higher molecular weight hydrocarbons, elemental sulphur, and sometimes helium and nitrogen.

The primary component of natural gas is methane (CH_4), the shortest and lightest hydrocarbon molecule. It also contains heavier gaseous hydrocarbons such as ethane (C_2H_6), propane (C_3H_8) and butane (C_4H_{10}), as well as other sulfur containing gases, in varying amounts, see also natural gas condensate. Natural gas also contains and is the primary market source of helium

2.4.1 Methane

Recent research concerning Catalytic Partial Oxidation (CPO) process has been focused on methane, as it is today the major feedstock for the production of hydrogen by steam reforming process on Ni catalysts Methane has the highest H/C ratio and thus is the most obvious source for hydrogen. Literature data indicate that in CPO of methane, Ni-based systems give high syngas yields but require operation at low temperatures to reduce metal loss, while Pt shows very stable performance but lower H_2 selectivity (Dissanayake, 1991).

The partial oxidation of methane is based on the following exothermic reaction:

$$CH_4 + 1/2O_2 \rightarrow CO + 2H_2, \quad \Delta H = -35.6 kJ/mol. \qquad [2.4]$$

However, CH_4 and O_2 at high temperatures are involved in many reactions giving principally CO, CO_2, H_2 and H_2O as products, and the composition of the final mixture depends on temperature, pressure, input gas composition and kinetics.

2.5 Catalytic combustion

2.5.1 Catalytic combustion of hydrogen

Catalytic combustion for hydrogen enables hydrogen combust easily at a relatively low temperature whereat does not reach flame combustion. For the purpose of eliminating this difficulty and in due consideration of the fact that hydrogen is more readily combustible than any other fuel, attempts have been made to develop a catalyst which enable combustion of hydrogen to proceed safely at low temperatures. (Haruta et al 1981).

Catalytically stabilized combustion (CST) provides the best available low-NO_x combustion technology, with demonstrated NO_x emissions less than 3 ppm (Beebe, 2000). In CST partial fuel conversion is attained catalytically (heterogeneously) and the remaining fuel is combusted in a follow-up homogeneous (gas phase) combustion zone. The heterogeneous combustion is a flameless process and does not contribute to NO_x, which is formed only via the homogeneous reaction pathway. CST is, therefore, a NO_x-preventing technology, resulting in a significant cost reduction compared to NO_x-after treatment techniques (SCR or SCONOX). The CST research activities are internationally intensified, driven by the stringent NO_x emission regulations in Europe and the United States (non-attainment areas in the United States already impose a 3 ppm NO_x limit). CST has been recently commercialized in small-scale (1.5 MW) gas turbines in the United States and current efforts focus on large-scale machines.

Further advancement in CST technology requires the development of catalysts with improved activity (desired light-off temperature less than 450°C) and thermal stability, understanding of the catalytic surface processes, knowledge of low-temperature homogeneous kinetics and their respective coupling with heterogeneous kinetics. The catalytic reactor in power generation systems consists of a multitude of large surface-to-volume ratio catalytically coated channels, necessitating

multidimensional numerical models with capabilities of detailed hetero/homogeneous chemistry, transport, and flow description. These models could be used to predict issues of practical interest, such as light-off characteristics, the likelihood of homogeneous ignition, and the attained fuel conversion within the catalytic reactor.

Heterogeneous kinetic studies of simple fuels such as H_2, CO and CH_4 over Pt or Pd have progressed substantially over the last years, *e.g.*, Hellsing *et al.* (1991), Hickman and Schmidt (1993), Deutschmann (1996), and Aghalayam *et al.* (2000). In addition, multidimensional numerical models capable of treating detailed surface and gas-phase kinetics are now available (refer to Dogwiler (1998), Deutschmann and Schmidt (1998)). The onset of homogeneous ignition within the catalytic reactor is detrimental to the catalyst integrity (it can cause catalyst meltdown) and the knowledge of such an event is of prime interest to CST reactor design. The gas-phase ignition is strongly influenced by the hetero/homogeneous coupling (catalytic fuel depletion, radical adsorption/desorption reactions) and, therefore, its accurate prediction requires the use of validated hetero/homogeneous chemical reaction schemes. In Dogwiler (1998) and Dogwiler *et al.* (1999), the authors validated hetero/homogeneous reaction schemes in CST of CH_4/air mixtures over Pt, using a 2-D elliptic fluid mechanical model with elementary hetero/ homogeneous reaction schemes and experimental ignition characteristics from an optically accessible catalytic combustor. Mantzaras and Benz (1999) have provided analytical homogeneous ignition criteria in 2-D channel configurations that included dependencies on the relevant chemical, flow, transport, and geometrical parameters. Such criteria were further adapted to CH_4/air CST in Mantzaras et al. (2000) using the validated hetero/homogeneous schemes from Dogwiler (1998). Of particular interest in natural gas-fueled turbines is the concept of hydrogen- assisted CST. Addition of small amounts of H_2 in natural gas reduces the catalyst light-off temperature and improves the combustion stability by damping flame pulsations. Dobbeling and Griffin (1999) proposed partial catalytic oxidation of a fraction of the natural gas as a viable way of producing hydrogen in gas-turbine systems. The knowledge of hydrogen CST is, therefore, an important step in the understanding of hydrogen-assisted CST. In hydrogen-assisted CST, care has to be exercised to avoid

catalyst hot-spots and homogeneous ignition within the catalytic reactor: H_2 is a strongly diffusionally imbalanced fuel with a Lewis number Le H 0.3, resulting in superadiabatic surface temperatures (Pfefferle and Pfefferle, 1985), that could deactivate the catalyst and promote homogeneous ignition.

2.5.2 Catalytic combustion of methane

The production of energy by the combustion of methane and natural gas is well established. Overall, the reaction may be represented by the equation

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \qquad \Delta H_{298} = -802.7 \text{ kJ/mol}$$

This overall equation is, however, a gross simplification with the actual reaction mechanism involving very many free radical chain reactions. Gas-phase combustion can only occur within given flammability limits, and the temperatures produced during combustion can rise to above 1600 °C, where the direct combination of nitrogen and oxygen to unwanted nitrogen oxides could occur.

Catalytic combustion offers an alternative means of producing energy. A wide range of concentrations of hydrocarbon can be oxidized over a suitable catalyst, and it is possible to work outside the flammability limits of fuel. Reaction conditions can usually be controlled more precisely, with reaction temperatures being maintained below 1600°C. This may be important both to minimize the production of nitrogen oxides and also to avoid thermal sintering of the catalyst. The catalytic combustion of methane is somewhat more complicated, as a result the fact that it is necessary to initiate oxidation at quite a high temperature. Once the reaction starts, subsequent oxidation is rapid and the heat release is considerable. As a result, it is more difficult to control temperature below the desired maximum.

With natural gas, it is somewhat easier to control temperature, since the presence of overall amounts of higher hydrocarbons allows initiation of oxidation at lower

temperatures. Thus, for example, the light-off temperature of methane at an air: fuel ratio of 5.3 is 368^{o}C; for ethane, the corresponding value is 242^{o}C. Once the higher hydrocarbon starts to oxidize, the heat liberated is sufficient to heat up the system and to initiate the oxidation of methane. Obviously, this depends on the fact that there is sufficient higher hydrocarbon to supply the heat required. The main focus of this article is on the chemistry of methane, but it is useful to remember that the use of natural gas can introduce some change. The combustion of methane can produce carbon dioxide or carbon monoxide, depending on the air: methane ratio:

$$CH_4 + 2O_2 \rightarrow CO_2 + 2H_2O \quad (1.1)$$

$$CH_4 + 3/2\ O_2 \rightarrow CO + 2H_2O \quad (1.2)$$

Other reactions may also be involved to a greater or less extent. These could include steam reforming (1.3) and (1.4) and the water shift (1.5) reactions:

$$CH_4 + 2O_2 \rightarrow CO + 3H_2 \quad (1.3)$$

$$2H_2 + O_2 \rightarrow 2H_2O \quad (1.4)$$

$$CO + H_2O \rightarrow CO_2 + H_2 \quad (1.5)$$

It is shown that the most effective catalysts are based on precious metals and over such systems; steam reforming becomes important at temperature in excess of 550^{o}C well within the range of catalytic combustion. The equilibrium of the water gas shift reaction has been well studied. Values of the equilibrium constants have been listed over a range operational conditions but the approach to equilibrium depends on the catalyst in use. Generally, higher temperatures favor the formation of carbon monoxide. Thus, it is necessary to consider the possibility of reactions other than (1.1) and (1.2).

The general pattern of catalytic combustion of hydrocarbons is well established (Figure 1). As temperature is increased, oxidation is initiated at a temperature that depends on the hydrocarbon and the catalyst.

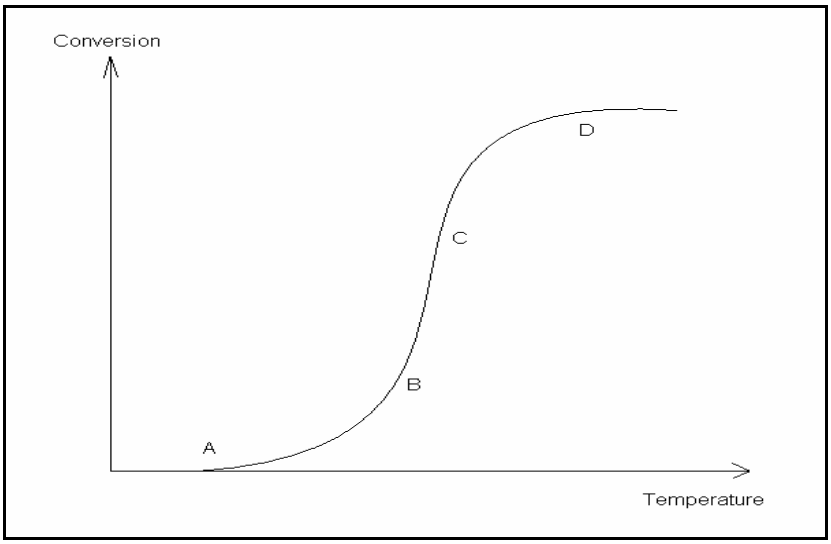

Figure 2.8: Conversion versus temperature in catalytic combustion.

A further increase in temperature leads to an exponential increase in rate (area B in Figure 2.8) to the point where heat generated by combustion is much greater than heat supplied. The reaction becomes mass transfer controlled (area C) until the reactants are depleted (area D in Figure 2.8).

One important factor in the catalytic combustion of hydrocarbons is 'light-off'. This can be defined in various ways but refers to the temperature at which mass transfer control becomes rate controlling. Because of the shape of the curve (Figure 2.8), the definition of light-off temperatures at which conversion reaches 10%, 20% or 50% makes little difference. It is also seen that the kinetics of catalytic combustion are only relevant to parts A and B of Figure 1. Once light-off occurs, mass and heat transfer are the important parameters. The geometry of the catalytic combustor together with the porosity of the catalyst/support has much more effect in this region.

The reaction rapidly approaches complete conversion of one or both reactants (Figure 2.8), and the heat generated from the combustion results in a significant increase in catalyst temperature. Thus, the stability of catalyst at high temperatures is also considerable interest. It is possible to design devices in which efficient heat transfer is used to minimize temperature rise (e.g. the catalytic boiler) but particular attention must

be paid in all cases to the temperature stability of materials. Thus, it is clear that considerations of catalytic combustion must include the chemical reactivity of the catalyst and the hydrocarbon (areas A and B), mass and heat transfer effects (area C) and maximum temperatures reached (relevant to area D). In some cases, further complexity may result from initiation of homogeneous combustion by overheating the catalyst. The present article considers mass and heat transfer effects only briefly, but relevant references are provided. Rather, attention is focused on the oxidation of methane on various catalysts in the presence of supports.

2.6 Flammability limit

2.6.1 Flammability limit of hydrogen

The flammability range of a gas is defined in terms of its lower flammability limit (LFL) and its upper flammability limit (UFL). The LFL of a gas is the lowest gas concentration that will support a self-propagating flame when mixed with air and ignited. Below the LFL, there is not enough fuel present to support combustion; the fuel/air mixture is too lean.

The UFL of a gas is the highest gas concentration that will support a self-propagating flame when mixed with air and ignited. Above the UFL, there is not enough oxygen present to support combustion; the fuel/air mixture is too rich. Between the two limits is the flammable range in which the gas and air are in the right proportions to burn when ignited.

A stoichiometric mixture occurs when oxygen and hydrogen molecules are present in the exact ratio needed to complete the combustion reaction. If more hydrogen is available than oxygen, the mixture is rich so that some of the fuel will re-main unreacted although all of the oxygen will be consumed. If less hydrogen is available

than oxygen, the mixture is lean so that all the fuel will be consumed but some oxygen will remain. Practical internal combustion and fuel cell systems typically operate lean since this situation promotes the complete reaction of all available fuel.

One consequence of the UFL is that stored hydrogen (whether gaseous or liquid) is not flammable while stored due to the absence of oxygen in the cylinders. The fuel only becomes flammable in the peripheral areas of a leak where the fuel mixes with the air in sufficient proportions.

Two related concepts are the lower explosive limit (LEL) and the upper explosive limit (UEL). These terms are often used interchangeably with LFL and UFL, although they are not the same. The LEL is the lowest gas concentration that will support an explosion when mixed with air, contained and ignited.

Similarly, the UEL is the highest gas concentration that will support an explosion when mixed with air, contained and ignited. An explosion is different from a fire in that for an explosion; the combustion must be contained, allowing the pressure and temperature to rise to levels sufficient to violently destroy the containment. For this reason, it is far more dangerous to release hydrogen into an enclosed area (such as a building) than to release it directly outdoors.

Hydrogen is flammable over a very wide range of concentrations in air (4 – 75%) and it is explosive over a wide range of concentrations (15 – 59%) at standard atmospheric temperature. The flammability limits increase with temperature as illustrated in Figure 1-6. As a result, even small leaks of hydrogen have the potential to burn or explode. Leaked hydrogen can concentrate in an enclosed environment, thereby increasing the risk of combustion and explosion. The flammability limits of comparative fuels are illustrated in Figure 2.8.

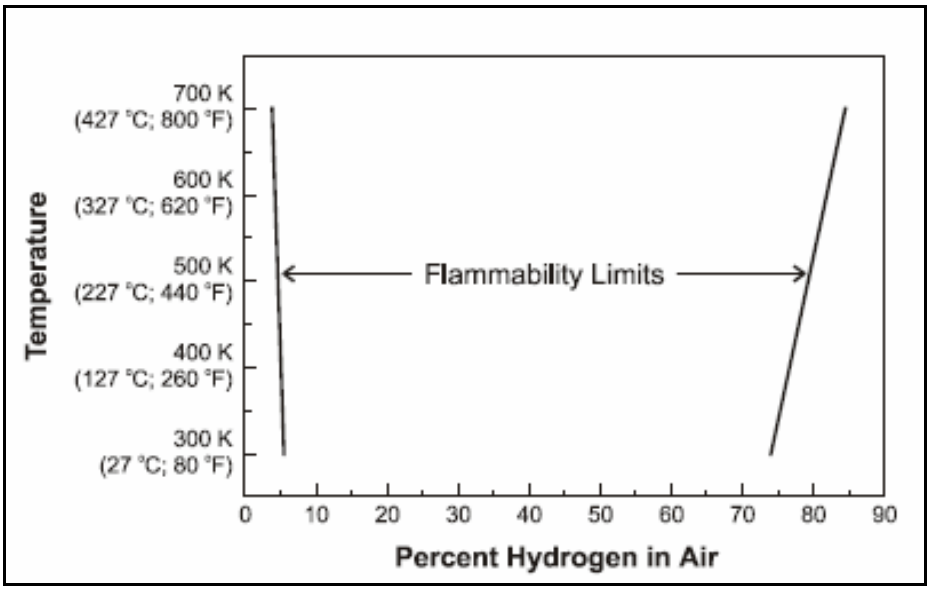

Figure 2.9: Variation of Hydrogen Flammability Limits with Temperature.

2.7 Autoignition temperature

The autoignition temperature is the minimum temperature required to initiate self-sustained combustion in a combustible fuel mixture in the absence of a source of ignition. In other words, the fuel is heated until it bursts into flame. Each fuel has a unique ignition temperature. For hydrogen, the autoignition temperature is relatively high at 1085ºF (585ºC). This makes it difficult to ignite a hydrogen/air mixture on the basis of heat alone without some additional ignition source (Andre, 2001).

2.8 Chemistry for hydrogen autoignition

The flammability of hydrogen is central to hazard considerations associated with its possible use as an energy carrier (Molkov *et al*., 2006). Safety assessments are affected by the chemical kinetics of its combustion (in addition to its unique buoyant